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Valence state analysis of Er in $CaZrO_3$

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1 Introduction

Recently, upconversion type ceramic phosphors was found, which can emit visible light excited by infra-red rays. Among such materials, Er-doped $CaZrO_3$ can emit green light by absorbing the near infra-red rays [1], whose emission intensity can be enhanced and color changes to yellow by additional doping of Yb. Although these phenomena are quite interesting, the mechanism of them have not yet been understood well. In the current study, valence state of the doped rare-earth ions, which is essential to discuss the electronic structure of the materials, were investigated by using the X-ray absorption near-edge structure measurements at rare-earth L_3 edges.

2 Experiment

All the sample specimens were fabricated with the conventional solid state reaction method using high purity powders of $CaCO_3$, ZrO_2, Er_2O_3 and Yb_2O_3 changing the concentration of doped Er and/or Yb. Crystal structures of synthesized materials were examined with the powder X-ray diffraction technique. Diffuse reflectance spectra in UV-Vis region were also observed for all samples to investigate the energy level structures around the band gap. Luminescence spectra were collected by using the near infra-red laser (980 nm, 0.25W).

XANES measurements were carried out at BL12C of Photon Factory in KEK, Tsukuba, Japan, in a transmission mode.

3 Results and Discussion

Observed XRD patterns of Er and/or Yb doped $CaZrO_3$ here synthesized show only the peaks originating orthorhombic perovskite structured $CaZrO_3$. It is noted here that both of the cation sites, i.e., Ca^{2+} and Zr^{4+} sites, can be replaced by Er and Yb ions with the ratio of 1:1. Observed diffuse reflectance spectra of Er or Yb doped $CaZrO_3$ are shown in Fig. 1. No sharp absorption peaks appear in Yb doped $CaZrO_3$, whereas there exist a lot of sharp absorption peaks in the case of Er-doped one. Photoluminescence spectra induced by infra-red lasers show green and yellow (green+red) emissions. Observed Er-L_3 XANES spectra are shown in Fig. 2, which suggests doped Er ions exist as trivalent ions. Summarizing above results with some additional investigations with theoretical calculations, Er plays a crucial role for green light emission and Yb gives another color, i.e., red, emission. It has been confirmed here by the L_3-edge XANES measurements that both of the doped Er and Yb ions are trivalent in $CaZrO_3$.

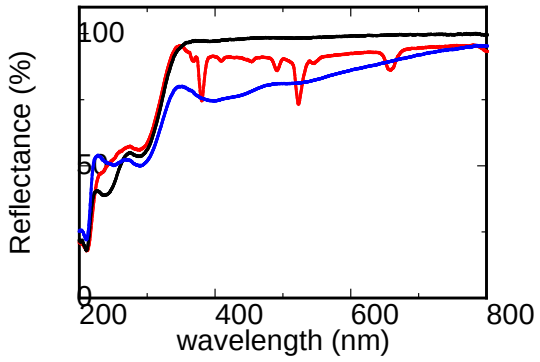

Fig. 1. Observed diffuse reflectance spectra of non-doped (black), Er-doped (red) and Yb-doped (blue) $CaZrO_3$.

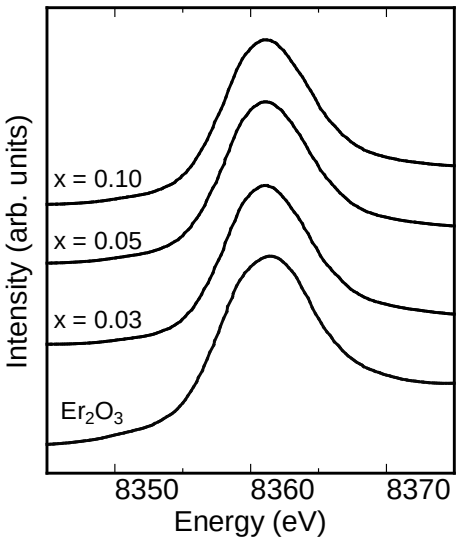

Fig. 2: Observed Er-L_3 XANES spectra of $Ca_{1-x/2}Er_xZr_{1-x/2}O_3$ and Er_2O_3.

References

[1] V. Singh *et al.*, *J. Appl. Phys.* **112**, 063105 (2012).

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